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Continuous CO_2 Capture in Dual Fluidized Beds Using Silica Supported Amine

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Abstract

In this study, a supported amine sorbent was prepared by impregnating silica particles (150~300 um) with methanol solution of polyethylenimine (PEI with the molecular weight of 600 $g \cdot mol^{-1}$) to immobilize amine into the pores of the silica support. The optimal CO_2 capacity of the PEI-based sorbent was as high as 2.0 $mmol \cdot g^{-1}$. During the adsorption and desorption of 10 times, the CO_2 capacity of the PEI-based sorbents kept stable, indicating PEI-based sorbents had excellent thermal stability.

Dual bubbling fluidized bed reactors were constructed to demonstrate the process feasibility of continuous CO_2 capture from flue gases with supported amine sorbent. Long-term stable operation and continuous solids circulation between the two reactors was achieved, and the CO_2 in the flue gases was continuously captured by the supported amine sorbent. Experimental results indicated that ~84.4% CO_2 capture efficiency could be achieved in the absence of water. The low regeneration temperature, high adsorption temperature and the short sorbent residence time in absorber were considered to be the limiting factors affecting the working capacity of sorbents. Water vapour could promote the adsorption process and increase the CO_2 capture efficiency to approximately 90.6~97%. The effect of water vapour on reaction mechanism between CO_2 and various amine groups was discussed.

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Keywords: CO_2 capture ; dual fluidized beds; supported amine; water vapour; mechanisms

1. Introduction

In recent years, much attention has been paid on the emission reduction of carbon dioxide concerning about potentially dangerous changes in climate[1]. An approach to reduce CO_2 release from large point sources is CO_2 capture and storage (CCS). The estimated costs for CO_2 transportation (US$1-3 per ton per 100 km)[2] and storage (US$4-8 per ton of CO_2)[2] are small compared to the cost of CO_2 capture,

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estimated at minimally US$35-55 per ton of CO_2 captured[3]. Therefore, reducing the cost of CO_2 capture is absolutely necessary to make CCS more economically attractive. The high cost of CO_2 capture stems from the considerable amount of energy required in the separation process[3].

Aqueous alkanolamine solutions are widely used to date in the gas processing industry for the removal of CO_2[4, 5]. However, this wet scrubbing system is energy intensive due to much heat needed for the regeneration of large amount of solvent. Furthermore, the solution slowly degrades and causes corrosion of the equipment. To overcome these shortcomings, amines immobilized on solid support by grafting or wet impregnation have attracted the attention of many researchers[6-11] in recent years.

Most researchers have been focusing on improvement of adsorption capacity applying various amine groups on mesoporous supports under different conditions. Ahn and his co-workers[12] investigated PEI-impregnated a series of mesoporous silica materials, MCM-41, MCM-48, SBA-15, SBA-16, KIT-6 to evaluate the CO_2 adsorption-desorption behaviours with the highest adsorption capacity of 3.07 mmol•g^{-1}. Qi et al.[13] developed nanocomposite sorbent based on oligomeric amine (PEI, TEPA) functionalized mesoporous silica capsules with the highest adsorption capacity of 7.9 mmol•g^{-1} under simulated humid flue gas at 75℃. Besides, Huang[14] found that the presence of water vapour doubled the amount of CO_2 adsorbed applying tetraethoxysilane modified MCM-48. Hiyoshi[11] reported that the amount of CO_2 adsorbed was almost the same for both in the presence of and in the absence of water vapour using aminosilane grafted SBA-15. The effect of water vapour during gas-solid adsorption interaction is of great importance because there is some water vapour in the content of flue gas or nature gas mixtures. But the effect of water vapour on the adsorption mechanism between amine groups and CO_2 has not been described in detail.

CO_2 capture using supported amine sorbent is an emerging post-combustion capture technology. Despite the increasing number of published works that deal with this topic, unfortunately, most of these studies have focused on sorbent material development and test using thermogravimetric analyzers, or fixed bed reactors. Alesi.et al.[15] evaluated the characteristic of a primary amine-functionalized polymeric ion-exchange resin in a packed bed reactor with the mass of 0.6~5.8g. Huang[14] studied the effect of water vapour in a fixed bed reactor.

In the CO_2 capture process with supported amine sorbent, the CO_2 sorbent circulates between the absorber and the regenerator, and the dual fluidized bed reactors being connected by solids transport lines will be a suitable system. Therefore, the dual fluidized bed reactors are the key technology to fulfil a continuous CO_2 capture. Recently, Veneman and Li[16] reported the continuous CO_2 capture by circulating fluidized bed reactor (CFBR) using supported amine and approximately 56% of CO_2 introduced was captured from simulated dry flue gas. However, there is still a lack of sufficient information about the CO_2 capture using supported amine sorbent with dual fluidized bed reactors. This paper describes continuous CO_2 capture from flue gases in dual fluidized bed reactors using supported amine sorbent to study the adsorption and desorption characteristics of supported amine sorbent in the continuous process.

Thus, the objective of the present work is to investigate the behaviour of supported amine in a dual fluidized beds system including fluid dynamics and heat transfer. High CO_2 capture efficiency is obtained in the presence of and in the absence of water vapour and the reaction mechanism between amine groups and CO_2 is analyzed with/without water vapour.

2. Experimental

2.1 *Sorbent preparation*

Commercial silica gel with mean pore diameter of 10 nm (CARIACT Q-10, 100~300 μm) and BET surface area of 273 m^2•g^{-1} and pore volume of 1.23 cm^3•g^{-1} was supplied by Fuji Silica Chemical Ltd as

the support material. Polyethylenimine (PEI) (linear type, b.p of 250℃) with the average molecular weight of 600 g•mol^{-1} came from Aldrich of Japan. PEI functionalized silica gel was prepared by wet impregnation according to the procedure[9] reported. In a typical preparation, 5 ml PEI was dissolved in 40 ml methanol under stirring for about 15min, after which 10 g dried Q-10 was added to the PEI/methanol solution. The slurry was continuously stirred for 2 h and then dried at 100℃ for 10 h.

2.2 Cyclic adsorption capacity in TGA

The cyclic adsorption capacity of the supported amine was studied in thermogravimetric analyzer. Approximately 10 mg of supported amine was placed in a platinum crucible and then heated at 100℃ and kept for 30min in N_2 atmosphere at the flow rate of 100 ml•min^{-1} to remove the moisture in sorbent. Then the temperature was reduced to 60℃ for 30 min, at which the adsorption was carried out under 10%CO_2+90%N_2 atmosphere. After adsorption , pure N_2 was input and the temperature was increased to 105℃ to regenerate the sorbent for 15min. Adsorption-desorption process in 10 cycles was carried out as this process above.

2.3 Dual fluidized bed system description

As Fig.1. shows the dual fluidized bed system includes the absorber (1) which is one bubbling bed ; the riser(2), one fast fluidized bed as the transport line; one high-efficiency cyclone separator (3) to recycle the solid material and release exhaust gas through the outlet; upper and lower loop seals (4)(6) to transport the material and control solid circulation rate and the regenerator(5) which is also one bubbling bed. Bubbling fluidized bed was selected as the absorber and regenerator to improve the gas-solid contact to increase reaction efficiency and regeneration extent. The exhaust gas out of the regenerator and the cyclone is introduced into one water washing vessel (7) to dissolve the amine vapour caused by the evaporation. CO_2 concentration out of cyclone is monitored by gas analyzer and temperature of the regenerator, the lower loop seal and absorber is measured by thermocouples. The system is operated under at atmospheric pressure and transport lines are used to connect different parts. The absorber is a circular column with the insider diameter of 50 mm and height of 260 mm, which is cooled by circulating cold water. The riser is also a circular column of 20 mm in inner diameter and 1720 mm in height. The cylinder section of cyclone is 100 mm in inside diameter and 345 mm in height with the gas outlet tube of 70 mm in inside diameter. The loop seal is rectangular with a cross section of 90×40 mm^2 and a height of 350 mm. Only the lower loop seal is cooled by circulating cold water. The regenerator is also a cylindrical column with the inside diameter of 50 mm and height of 692 mm. The regenerator is heated by circulating hot oil so that the column can be heated uniformly. Nitrogen is input as the fluidization gas in regenerator so that the sorbent can be regenerated at lower temperature (~110℃) , which is subjected to the smoke temperature (~150℃) of the employed oil. Secondary nitrogen is introduced at the bottom of the riser. Therefore, the steam of CO_2/N_2 mixture plus the secondary nitrogen transports the supported amine particles into cyclone and upper loop-seal. Then the particle flows into regenerator under the drive of pressure drop between two sides of the upper loop seal. The supported amine releases CO_2 in regenerator at high temperature and regains the capacity of adsorbing CO_2. Then the sorbent flows into the absorber through the lower loop seal. The gas from the absorber and the regenerator is introduced into one bubble vessel filled with water to wash the possible evaporated amine before emitting into atmosphere. Little of the exhaust gas from the cyclone outlet is directly sampled by on-line gas analyzer to monitor CO_2 concentration and estimate the CO_2 capture efficiency.

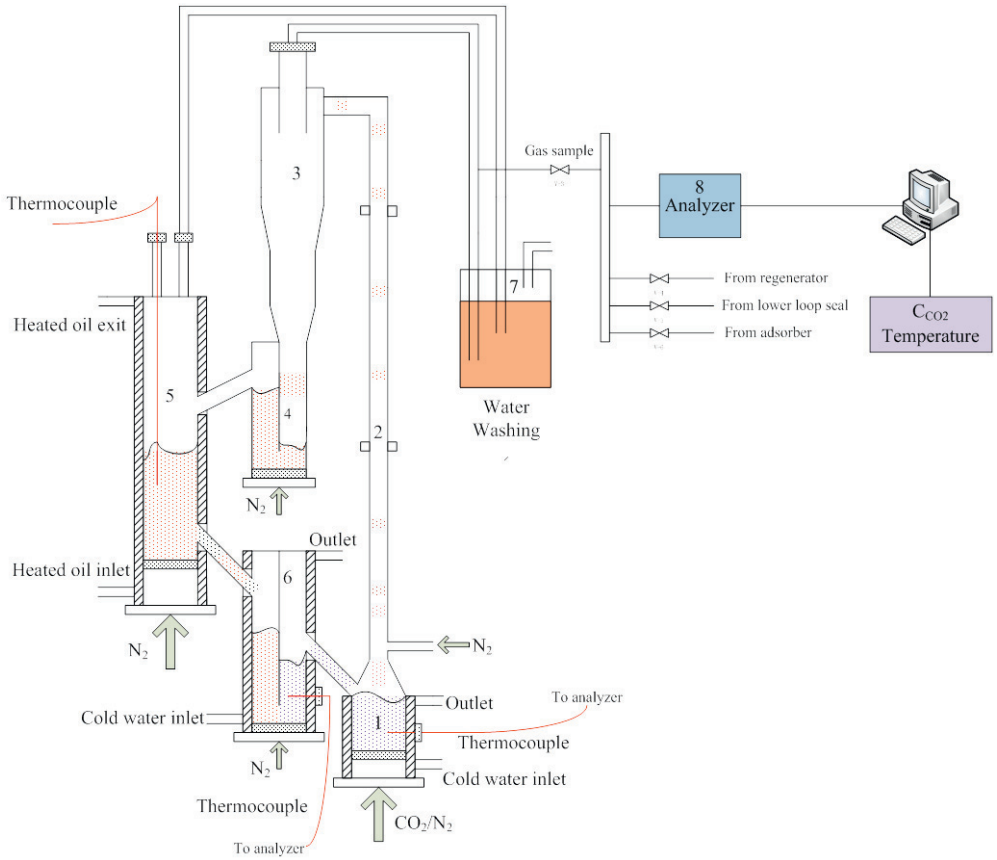


Fig. 1. Schematic diagram of dual fluidized bed system: (1) absorber; (2) riser; (3) cyclone; (4) upper loop seal; (5) regenerator; (6) lower loop seal; (7) gas washing and evacuation; (8) concentration and temperature analyzer.

3. Results and Discussion

3.1 *Cyclic stability of the supported amine*

The adsorption capacity of the supported amine in 10 cycles was displayed in Fig.2. Fig.2 (a) demonstrated the adsorption and desorption processes in 10 cycles. There was a slight decrease of the sorbent weight after complete regeneration every cycle. The sorbent weight decreased by approximately 0.6% after 10 cycles, which was caused by the evaporation of amine supported in the pore of silica gel. However, the cyclic adsorption capacity was 2.2 mmol·g^{-1} and kept stable in 10 cycles shown as Fig.2 (b). The cyclic adsorption capacity did not display any decrease with the loss of amine group because the slight evaporation of amine promoted the mass transfer between CO_2 in bulk gas and amine layer and more active sites of amine group were exposed. Therefore, for supported amine there existed one optimal loading amount of amines. However, the thermal stability would decrease with the rise of experiment temperature resulting in the drop of adsorption capacity.

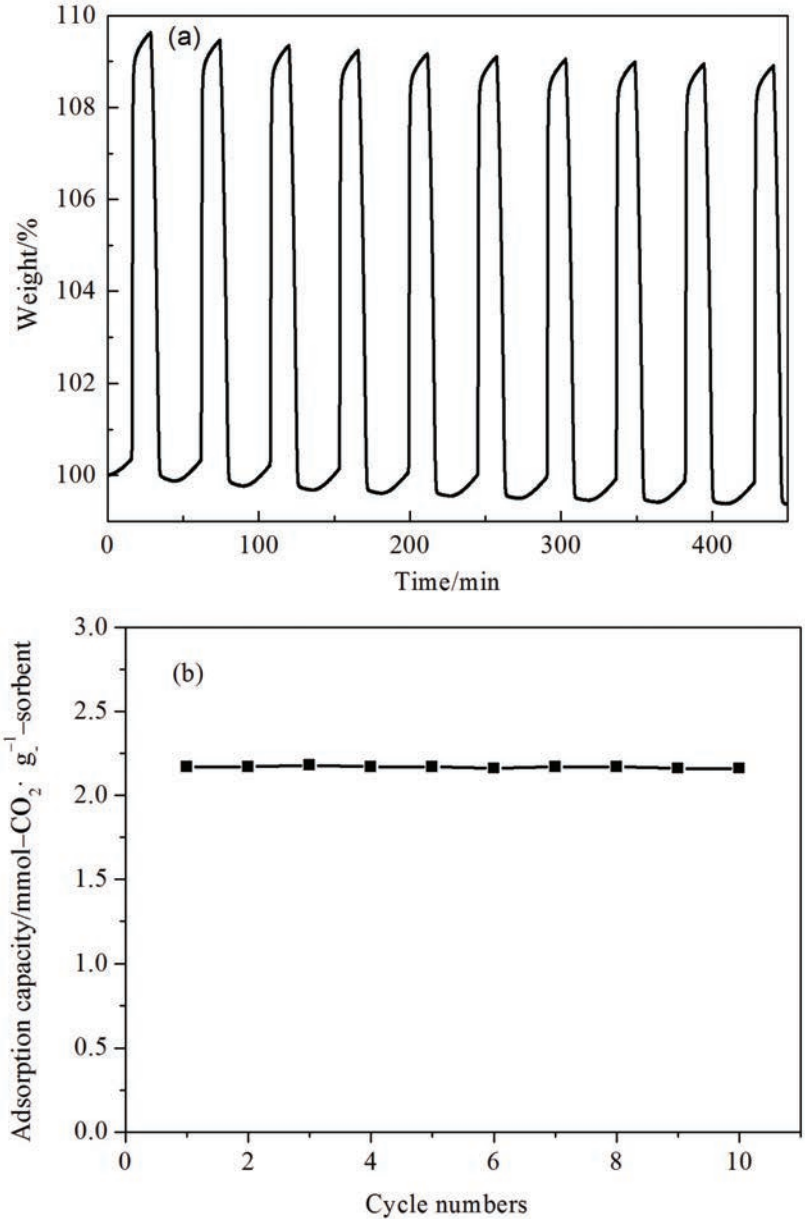


Fig.2 (a) adsorption-desorption processes in TGA between 60℃ and 105℃; (b) cyclic adsorption capacity with cycles

3.2 Continuous CO_2 capture experiment

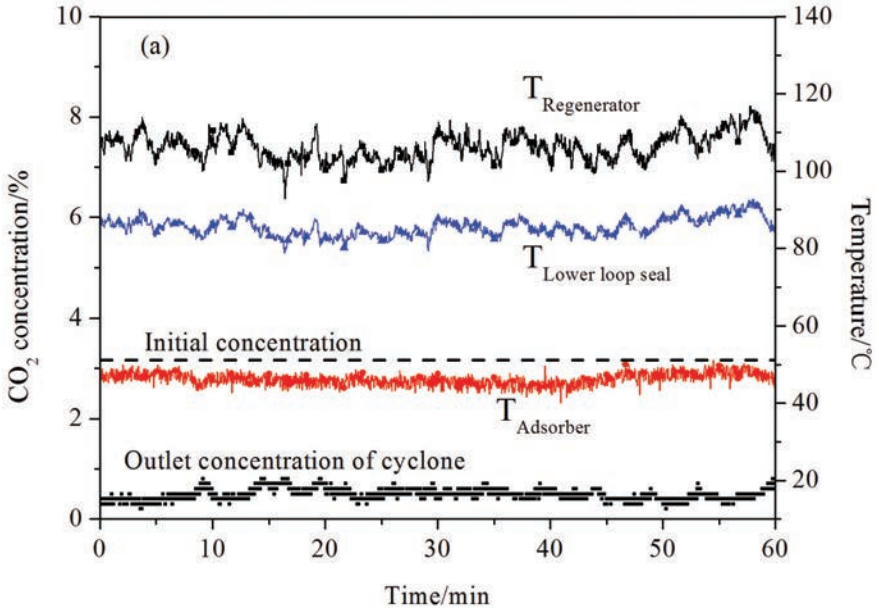
The flow rate of fluidization gas introduced was shown as Tab.1 when the dual fluidized bed system reached steady. The flow rate of CO_2 introduced was 60 $L \cdot h^{-1}$ (~44.6 $mmol \cdot min^{-1}$) and the initial concentration was measured to be 3.2% at ambient temperature. The solid circulating rate was evaluated to be approximately 50$g \cdot min^{-1}$.

Tab.1 Flow rate and atmosphere introduced into for dual fluidized bed

	Absorber		Riser	Upper loop seal	Lower Loop seal	Regenerator
	CO_2	N_2	N_2	N_2	N_2	N_2
Flow rate($L \cdot h^{-1}$)	60	500	400	400	150	300

After the system ran continuously and steadily, the outlet CO_2 concentration was monitored with time as Fig.3 showed. The outlet concentration was approximately 0.5%, and correspondingly the time averaged CO_2 capture efficiency was about 84.4%. CO_2 capture efficiency was determined by the circulating rate and working capacity of sorbent. According to the solid circulating rate analyzed previously, the working capacity was just approximately 0.8 $mmol \cdot g^{-1}$. The working capacity was subjected to the net adsorption capacity in absorber and regeneration extent which was affected by regeneration temperature. The net adsorption capacity in absorber depended on the adsorption temperature and residence time in absorber. As Fig.3(a) demonstrated, in regenerator the temperature of particle surface was about 110℃ with the residence time of 11 min.

However, there was some percentage of CO_2 in regenerator atmosphere which would inhibit the desorption of sorbent and reduce the regeneration rate resulting in incomplete regeneration. Furthermore, the sorbent temperature in lower loop seal was around 90℃ at which it was not suitable for supported amine to adsorb CO_2. The bed temperature measured in absorber was approximately 50℃, but in absorber the particles did not mix well. Therefore the real temperature of regenerated sorbent flowing into absorber and reacting with CO_2 should be between 50℃ and 90℃. Hence, the higher adsorption temperature due to limited heat transfer surface and efficiency may be the limiting factor for the low working capacity. Besides, lots of heat would be released during the rapid reaction between amine and CO_2. The heat released should be removed in time, otherwise it would lead to the increase of sorbent temperature. Therefore, the heat transfer issue should be considered seriously to control the adsorption temperature around 60℃. Conclusively regeneration temperature should be increased and the sorbent flowing out of regenerator should be cooled down as soon as possible by increasing heat transfer surface. Therefore for dual fluidized bed experiment, the performance of solid fluid dynamics was perfect, but the main problem was about heat transfer and temperature control.



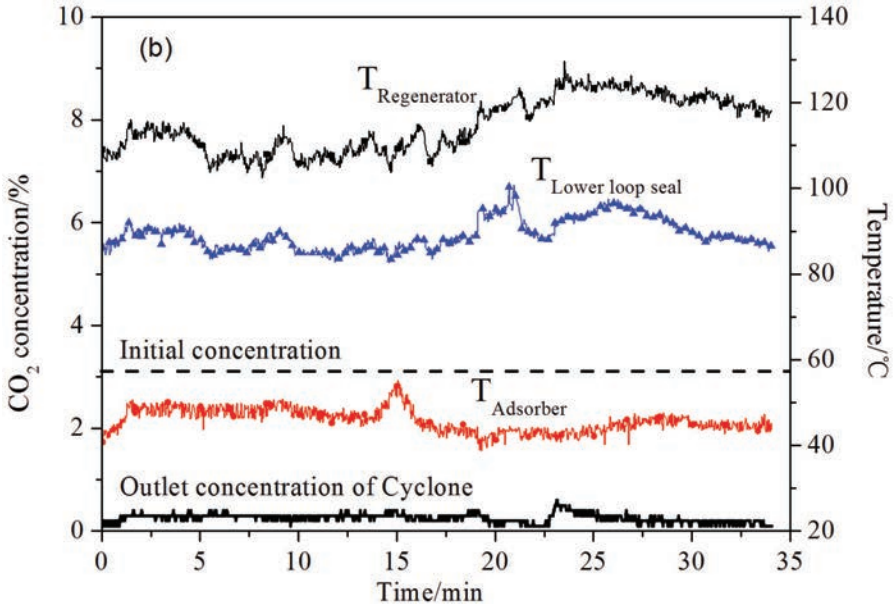


Fig.3 CO_2 concentration out of cyclone and temperature in regenerator, lower loop seal and absorber (a) without water vapor; (b) with water vapor.

From the reactor point of view, for the absorber, fast fluidized bed will be the best option; for the regenerator, bubbling fluidized bed or moving bed will be suitable. Considering equilibrium and kinetics, a high regeneration temperature is required in order to regenerate fully the amine sorbent. The cooling of hot sorbent from the regenerator and removing the heat released in the absorber are necessary. The control of sorbent particle circulation rate between two reactors is critical because this will affect significantly the heat requirement for sorbent regeneration and the capture efficiency.

Fig.3 (b) displayed the effect of water vapour on CO_2 capture efficiency. The outlet concentration was in the range of 0.1%~0.3%, and the CO_2 capture efficiency was calculated to be 90.6%~97%, which indicated water vapour promoted the adsorption of CO_2. However, the effect was not as significant as the result[14] Huang reported. Therefore, the effect extent of water vapour on various amine groups was different and the mechanism was analyzed as follows.

3.3 Mechanism of H_2O effect on the reaction between amines and CO_2

The reaction of amine groups with CO_2 can be governed by several different mechanisms. Primary, secondary and hindered (containing an amine functional group surrounded by a crowded steric environment) amines can react with CO_2 directly to yield carbamate through the formation of zwitterionic intermediates. The two-step zwitterionic mechanism given by Danckwerts[19] and derived from Caplow's work[20] successively involves the formation of a "wzitterion" and the subsequent removal of the proton by a base B (base catalysis) such as H_2O, amine molecule as Fig.4 shows. After the deprotonation of the zwitterions, the proton can be bonded with free amine to yield carbamate or with H_2O to form carbonate. The production ratio depends on the reaction rate of the two pathways. Chaffee[21] observed the two phases, carbamate and carbonate, and pointed that the formation of carbonate was much slower than the yield of carbamate. Besides, kenig[22] found similar results for CO_2 adsorption with aqueous amines, which depicted the kinetic constant k_2 was much lower than k_1 in eq.(1). As to supported amine, the water

vapour was entrained by gas steam. Therefore, compared with aqueous amines, the concentration of H_2O was much lower for supported amine. Hence, for the reaction of primary and secondary amines and CO_2, the production is mainly carbamate with very little carbonate even at moisture atmosphere. In other words, effect of moisture on the adsorption promotion of primary and secondary amines is slight.

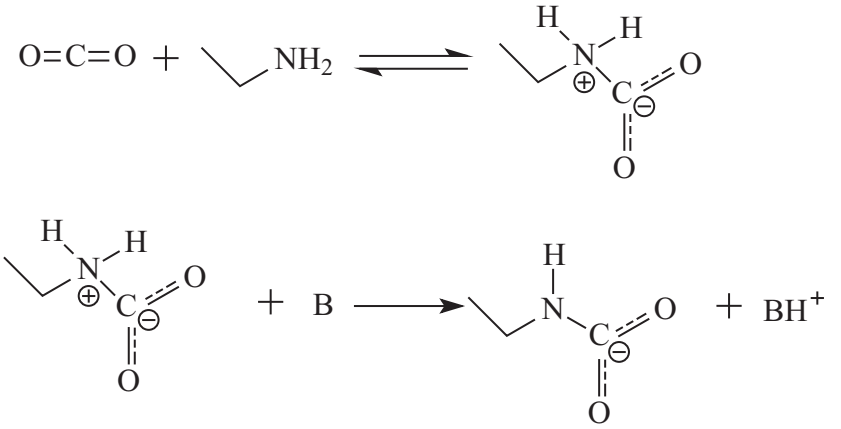
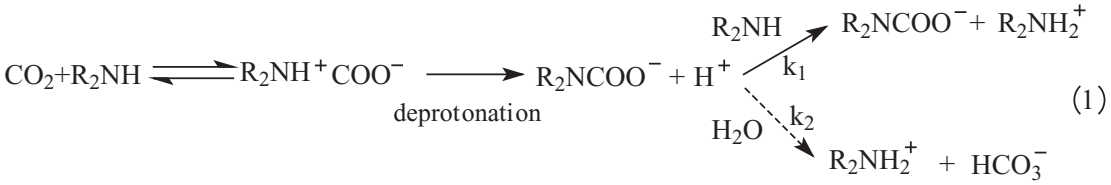


Fig. 4 Carbamate formation mechanism of reaction between CO_2 and primary, secondary and hindered amines.

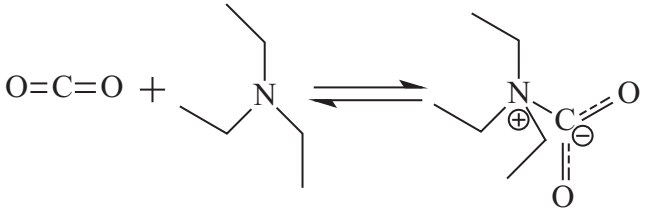


(1)

However, tertiary amine groups cannot react with CO_2 directly. As Donaldson and Nguyen suggested[23], such amines have a base-catalytic effect on the hydration of CO_2, given[22] as eq.(2).

(2)

In principle, the base-catalytic effect can be explained by different mechanisms[22]. A zwitterions-type mechanism earlier proposed by Yu and Astarita[24] can be employed for supported amine. The bicarbonate is yielded through the reaction of water and zwitterions-type complex demonstrated as Fig.5. Therefore, water is essential for tertiary amines to react with CO_2.



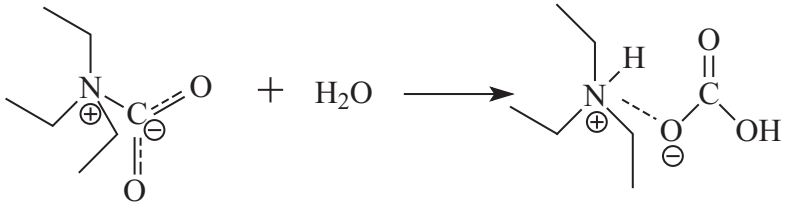


Fig. 5 Zwitterions-type mechanism of reaction between CO2 and tertiary amines.

According to the analysis above, moisture will increase the adsorption capacity of supported amines containing tertiary amine groups. PEI has about 30% of primary amine, 40% of secondary amine with the left (~30%) of tertiary amine[25]. Therefore, there was some extent of increase for the CO_2 capture efficiency after water vapour was entrained in as Fig.3(b) showed.

4. Conclusions

The dual fluidized bed system was built to simulate continuous CO_2 capture applying PEI modified silica gel. The cyclic adsorption capacity of the supported amine was 2.2 $mmol \cdot g^{-1}$ and CO_2 capture efficiency of 84.4% was achieved during long time operation with the working capacity of just approximately 0.8 $mmol \cdot g^{-1}$. The working capacity was mainly subjected to the high adsorption temperature and short residence time in absorber. Therefore, the heat transfer issue was of great significance to supply sufficient heat for regeneration, cool down the regenerated sorbent in time and remove the heat released in absorber. Water vapour entrained into absorber increased the CO_2 capture efficiency to about 90.6%~97%. Furthermore, the effect of water on adsorption mechanisms was discussed. For supported amines, water had little adsorption promotion for primary and secondary amine groups because carbamate was much easier and faster to be yielded than carbonate. And tertiary amine could react with CO_2 only in the present of water. Therefore, water vapour may display obvious positive effect on amines containing lots of tertiary amine groups.

Acknowledgements

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